

GUIDANCE

UCMR Monitoring, Chemical Vulnerability, Cr(VI) Sample Collection and Preservation, and Screening for Cr(VI) with Total Chromium

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MONITORING DHS is working with the Sanitation and Radiation Laboratory and the Environmental Laboratory Accreditation Program to develop detection levels for purposes of reporting (DLRs) for the UCMR chemicals that do not have them and to see that laboratories are appropriately certified; as the DLRs are developed, they will become available on the DLR list posted on the DHS website <http://www.dhs.ca.gov/ps/ddwem/index.htm> under the menu item “electronic data reporting”. A list of laboratories with interim certification for Cr(VI) is available at <http://www.dhs.ca.gov/ps/ddwem/chemicals/Chromium6/Cr+6labs.htm>. When available, a list of methods will be added to the guidance posted on the website.

Monitoring requirements for chemicals that have been carried over from the previous list (perchlorate, 1,2,3-trichloropropane, dichlorodifluoromethane, ETBE, and TAME) can generally be satisfied by grandparenting data, as allowed under the new regulations. However, new sources that are vulnerable, and sources that are newly-designated as vulnerable to any of these must monitor. It may be possible to grandparent data for the new chemicals as well, if the samples were collected since January 1, 1998. Note that compositing for UCMR chemicals is no longer allowed.

VULNERABILITY

General Information If a drinking water source assessment has been completed or information is available about possible contaminating activities (PCAs) that could pose a risk of contamination to the source, that information must be considered in making the vulnerability determination. Some known PCAs of concern are listed below for each of the UCMR chemicals. In some cases, representative sampling may be appropriate, if approved by the Department. In addition, for hexavalent chromium, you may choose to do an initial screening using total chromium analysis as detailed below.

For *Ethyl-tert-butyl ether (ETBE)* and *tert-Amyl-methyl ether (TAME)*, source vulnerability is determined at this time by the presence of MTBE, since these chemicals are only used along with MTBE and at lower levels.

Hexavalent chromium Generally, all sources are considered vulnerable to hexavalent chromium unless a screening using total chromium analysis (see below) indicates by a nondetect that a source is not vulnerable. PCAs include:

- Use or manufacture of wood preservative formulations that include chromium compounds, e.g., potassium dichromate, chromic acid, and sodium dichromate.
- Industrial applications, e.g., automobile, appliance, and other consumer product manufacturing.

- Steel hardening, manufacturing of stainless steel and other alloys, chromium plating.
- Pigment making, leather tanning, welding.

In addition—due to the fact that water treatment facilities that use an oxidant (such as chlorine, ozone, or permanganate) may convert chromium-3 to chromium-6, DHS recommends that, for sources with detected chromium, chromium-6 analyses be performed on water samples taken after treatment, as well as before.

Boron Boron is a naturally-occurring element found in soil and water in the form of boric acid and sodium tetraborate; levels vary depending on geology of the area. PCAs include industrial waste discharges, particularly from tallow manufacturing.

Dichlorodifluoromethane PCAs include:

- Polymerization processes
- Food sterilization (fumigant solvent)
- Home and commercial refrigeration
- Paint and varnish remover manufacturing and use
- Water purification
- Copper and aluminum production
- Glass bottle manufacturing (petroleum recovery)
- Leak-detecting agent in thermal expansion valves
- Prior to 1979, frequently used as an aerosol propellant for cosmetics, pharmaceuticals, insecticides, paints, adhesives, and cleaners.

Perchlorate Perchlorate originates as a contaminant in ground and surface waters from the dissolution of ammonium, potassium, magnesium, or sodium salts. PCAs include

- Manufacturing and use of solid propellant in rockets, missiles, and fireworks
- Air bag inflator manufacturing
- Nuclear reactors and electronic tubes
- Manufacturing and use of lubricating oils, fabrics, dyes, rubber, paints, and certain fertilizers
- Leather tanning and finishing
- Electroplating and aluminum refining
- Hazardous waste sites

tert-Butyl alcohol (TBA) PCAs include fuel manufacturing and use (TBA is a fuel oxidant and also a metabolite of MTBE), and the manufacturing and disposal of some metallic and paperboard food containers, and hazardous waste sites.

1,2,3-Trichloropropane (TCP) 1,2,3-TCP has various industrial uses and historic pesticide uses. The primary PCA appears to be hazardous waste sites.

Vanadium Naturally-occurring; the primary PCA is steel manufacturing, but vanadium is also used in the manufacturing of phthalic anhydride, sulfuric acid, pesticides, dyes, inks, pigments, and other chemicals; has been found in association with hazardous waste sites.

RECOMMENDATIONS FOR HEXAVALENT CHROMIUM SAMPLE COLLECTION AND PRESERVATION

The method DHS specifies for the determination of Cr(VI) in drinking water is EPA method 218.6 “Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography”. As indicated in the title, this method was originally devised to be applicable to a broad range of aqueous samples, including industrial wastewaters, i.e., it was not primarily intended for the analysis of drinking water. As such, the method provides some latitude in terms of sample preservation and pretreatment, stipulating that consideration should be given to the type of data required.

Considering the specific situation with drinking water, the Department provides the following guidance with regard to sample filtration, pH adjustment, and sample transportation and storage:

(1) Filtration of samples immediately following sample collection is not recommended. Drinking water samples are typically low in particulate matter and performing filtration in the field without the potential of adsorption losses and/or contamination is difficult. Filtration of drinking water samples is also not performed in the determination of other trace metal contaminants. Filtration of samples immediately prior to the ion chromatographic determination is recommended in order to protect the analytical instrumentation, i.e., to avoid premature clogging of the guard column.

(2) Immediately following collection, the pH of samples should be adjusted to the range 9.0-9.5 in order to minimize the potential loss of Cr(VI) through chemical reduction.

With some water samples it may be difficult to achieve the desired pH with the ammonium sulfate/hydroxide buffer prescribed by EPA 218.6 (e.g., Colorado River water) without adding so much sulfate that the subsequent ion chromatographic analysis is compromised through analytical column overloading. For water samples exhibiting this problem, the Department suggests the use of a modified pH-adjustment buffer that contains ten times less ammonium sulfate (33 g/L) but the same concentration of ammonium hydroxide as the buffer prescribed in EPA 218.6. It should be noted however, that at the present time the Department does not have sufficient data to determine whether this modified buffer is adequate for all types of drinking water samples.

(3) Samples must be cooled to 4 °C during transport and storage and analyzed within 24 hours of collection.

SCREENING FOR HEXAVALENT CHROMIUM USING TOTAL CHROMIUM ANALYSIS

The Department’s present DLR for Cr(VI) is 1 µg/L. This value was originally derived from a single-laboratory MDL of 0.2 µg/L using a multiplier of five. In order to be consistent with the DLR for Cr(VI) of 1 µg/L, any analytical technique for measuring total chromium which is to serve as a screening tool for Cr(VI) must be capable of

achieving a total chromium reporting limit of 1 µg/L or better. The advantages of a total chromium screening approach are that

- (1) total chromium determinations are less costly, and
- (2) total chromium determinations are not subject to the short holding time constraints of the Cr(VI) method.

Of the atomic spectrometry techniques generally used for total chromium determinations, i.e., Flame-AAS, GFAAS, ICP-AES, and ICP-MS, only GFAAS and ICP-MS appear to have the potential to achieve the required RL. This is based on the results of the recent multi-analyte and multi-laboratory study performed by the Reporting Level Work Group (RLWG).

Utilities and their laboratories may use ICP-MS or GFAAS for initial screening for total chromium in lieu of performing the more time-consuming hexavalent chromium method (EPA 218.6). In order to use these screening tools, laboratories must demonstrate that they can analyze water samples at the 1 µg/L level with a precision (RSD) of 20% and an accuracy, as measured by percent recovery, in the range 80-120%. A method detection limit (MDL) must be established following EPA protocol (40CFR136 Appendix B). The reporting limit should be no less than three times the MDL. EPA approved methods for the analytical technology selected must be followed and all of the QC criteria specified in those methods must be met. Laboratories should maintain their QC criteria for review should any questions arise regarding the results and their adequacy for screening.

When samples yield screening results above 1 µg/L, the respective sources should be re-sampled as soon as practically possible and analyzed by EPA method 218.6 for Cr (VI).

NOTE: Labs using ICP-MS should digest the samples to avoid any positive interference by carbon that can occur in the analysis of Total Chromium.